

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.

THIS PAGE BLANK (USPTO)

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | | |
|---|--|--|--|
| (51) International Patent Classification ⁶ : | | (11) International Publication Number: | WO 98/28399 |
| C11D 17/04, 1/94, 1/37, 3/20, 3/50, A47L 13/17 | | A1 | (43) International Publication Date: 2 July 1998 (02.07.98) |
| (21) International Application Number: PCT/EP97/06960 | | (74) Agent: ELLIOTT, Peter, William; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB). | |
| (22) International Filing Date: 4 December 1997 (04.12.97) | | (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). | |
| (30) Priority Data: 9626622.6 20 December 1996 (20.12.96) GB | | (71) Applicant (for AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). | |
| (71) Applicant (for all designated States except AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG US ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). | | (72) Inventors; and (75) Inventors/Applicants (for US only): RENNIE, George, Kerr [GB/GB]; 26 Spital Road, Bebington, Wirral, Merseyside L63 9JF (GB). REVELL, Patricia [GB/GB]; 38 Bickerton Avenue, Higher Bebington, Wirral, Merseyside L63 5NB (GB). SAMS, Philip, John [GB/GB]; Cranford, Briardale Road, Willaston, South Wirral, Cheshire L64 1TB (GB). | |
| (54) Title: IMPROVEMENTS RELATING TO SURFACE CLEANING | | | |
| (57) Abstract | | | |
| <p>The invention comprises a kit of parts which comprises, in combination: a) a shaped article comprising a sponge body having a first surface defining a pouch therein, said pouch being adapted to receive and retain a surfactant-containing composition, and, b) a surfactant-containing composition which comprises a particulate phase. The invention also relates to a method of surface cleaning using a sponge body having a first surface defining a pouch therein, said pouch being adapted to receive and retain a surfactant-containing composition which comprises the steps of: a) at least partially filling said pouch with a surfactant containing composition which comprises a particulate phase, and, b) performing a manual cleaning operation with the sponge.</p> | | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|----|--------------------------|----|---------------------------------------|----|---|----|--------------------------|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Switzerland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GB | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | ML | Mali | TR | Turkey |
| BG | Bulgaria | HU | Hungary | MN | Mongolia | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MR | Mauritania | UA | Ukraine |
| BR | Brazil | IL | Israel | MW | Malawi | UG | Uganda |
| BY | Belarus | IS | Iceland | MX | Mexico | US | United States of America |
| CA | Canada | IT | Italy | NE | Niger | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NL | Netherlands | VN | Viet Nam |
| CG | Congo | KE | Kenya | NO | Norway | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NZ | New Zealand | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | PL | Poland | | |
| CM | Cameroon | KR | Republic of Korea | PT | Portugal | | |
| CN | China | KZ | Kazakhstan | RO | Romania | | |
| CU | Cuba | LC | Saint Lucia | RU | Russian Federation | | |
| CZ | Czech Republic | LI | Liechtenstein | SD | Sudan | | |
| DE | Germany | LK | Sri Lanka | SE | Sweden | | |
| DK | Denmark | LR | Liberia | SG | Singapore | | |

- 1 -

IMPROVEMENTS RELATING TO SURFACE CLEANING

5 Technical Field

The present invention relates to improvements in surface
cleaning and will be described with particular reference to
hand dish washing and other forms of hard surface cleaning,
10 although the invention is also applicable to skin cleaning.

Background to the Invention

15 It is known to use sponges as carriers for surfactant during
cleaning processes. One difficulty with these processes, is
that the surfactant payload must be recharged at regular
intervals by contacting the sponge with a surfactant
containing composition, e.g. by dipping the sponge in a
20 surfactant solution, gel or powder or pouring surfactant
solution over the sponge.

It has been suggested to provide cleaning and wiping articles
which comprise integral surfactant. For example, EP 0353013
25 (Unilever: 1988) discloses a wiping article which comprises
two porous substrate layers sandwiching a body of surfactant,
while US 3949137 (Akrongold: 1974) discloses a gel-containing
pre-impregnated sponge. One difficulty with the above-
mentioned articles is that when the surfactant is exhausted
30 the article must be replaced as it is difficult to recharge
with surfactant without the use of an industrial process which
the common user of the product is not in a position to
perform.

- 2 -

In a known alternative, a sponge is attached to a hollow handle which acts as a container for a surfactant. The surfactant flows from the handle into the sponge during use providing a continuous supply of surfactant during the
5 cleaning process. These devices can be refilled in a more straightforward manner than those described above but are relatively complex and costly to manufacture.

GB 0979735 (Schermuly: 1963) discloses a cellulose sponge
10 with an aperture therein to receive and retain 'one or more pieces of soap which might otherwise have been discarded', together with a plug to close the aperture.

GB 1171180 (Sponcel Limited; 1965), GB 1216843 (Howian Investments: 1967) and GB 1245242 (Brennan: 1967) all disclose how a source of detergent can be included in a sponge by means of a recess which is cut into a sponge to receive a solid block of surfactant material or by forming a sponge around a detergent-containing body. These
20 contructions are not refillable.

US 4415288 (Gordon: 1981) discloses a medical scrub (which is shown in the figures as looking like a sponge with a slit in the side), together with a device for refilling an
25 aperture in the scrub with a fluid, which can contain soap and/or antiseptic solution.

It has also been proposed to use a dilution-thickening composition to assist retention of the cleaning
30 composition on a sponge or other such carrier. It is known to carry out a cleaning process which comprises the steps of:

- 3 -

- a) treating an adsorbent carrier with a surfactant composition which is capable of thickening on the addition of water,
- 5 b) treating the combination of the carrier and surfactant composition with water, and,
- c) subsequent to steps (a) and (b) performing a cleaning operation with the carrier.

10

A further problem with surfactant carriers, such as sponges, is that they can also carry soil, particularly greasy soil. This can present the difficulty that during prolonged use the carrier will become coated with grease and will consequently 15 re-deposit grease on surfaces which are being cleaned thus making the cleaning process far less efficient and eventually, quite pointless.

This is particularly important when the cleaning process is 20 performed at a relatively low temperature. It is known that to remove fatty soil from plates under hot bowl wash conditions, active levels lower than the critical micelle concentration of the surfactant (typically below 0.01%wt) may suffice. In contrast, under ambient conditions much higher 25 active levels (typically above 0.1%wt) are preferred to ensure fats are removed and stably dispersed. Lower levels of active may help removal at lower temperatures but fat removal is incomplete and build-up on the sponge occurs. Such built-up grease kills lather and can be transferred to both hands and 30 clean dishes. In this way it signals the exhaustion of the product to the user.

There remains a need for a simple and inexpensive sponge-like wiping and cleaning article which contains a supply of 35 surfactant which can be replenished with ease. Potential

- 4 -

difficulties with these composition occur when the composition contains components other than the surfactant and there is a need to ensure that these other components are also retained in the sponge.

5

Brief Description of the Invention

We have determined that several possible benefits arise from
10 the use of a sponge comprising a pouch to receive and retain a dilution-thickening surfactant-containing composition.

Accordingly the present invention provides, in combination,

- 15 a) a shaped article comprising a sponge body having a first surface defining a pouch therein, said pouch being adapted to receive and retain a surfactant-containing composition, and.
- 20 b) a surfactant-containing composition which comprises a particulate phase.

According to a further aspect of the present invention there is provided a method of surface cleaning using a sponge body
25 having a first surface defining a pouch therein, said pouch being adapted to receive and retain a surfactant-containing composition which comprises the steps of:

- 30 a) at least partially filling said pouch with a surfactant containing composition which comprises a particulate phase, and,
- b) performing a manual cleaning operation with the sponge.

- 5 -

A particular advantage of the present invention is that component release from the sponge is retarded by the use of a pouch and the composition. A benefit of this is that sufficient surfactant is retained in the sponge for effective
5 cleaning to be performed for a longer time. It is also believed that, the maintenance of a relatively high surfactant concentration within the body of the sponge, replenished from the pouch, significantly reduces the tendency of the sponge to transfer greasy soil between surfaces being cleaned.

10

The above benefits are attained when the surfactant containing composition is of rather simple composition, additional benefits accrue when the surfactant containing composition is of a more complex nature. As will be described below in
15 further detail, when abrasives are present in the composition the sponge acts as a filter to remove the larger abrasive particles which would scratch or otherwise damage the surface being cleaned. As will also be described below, it is envisaged that if other particulate forms such as encapsulated
20 perfumes, insoluble bleaches and germicides are incorporated into the surfactant containing compositions the release of these additional components is also retarded and extended.

25 Detailed Description of the Invention

Sponge:

Sponges for use in embodiments of the present invention may be
30 natural or synthetic. For synthetic sponges polymeric materials, including polyester and polyurethane are suitable. As is known in the art, the process and conditions of manufacture will determine the properties of the sponge. Property variables include pore size and pore size
35 distribution, pore shape, mechanical strength,

compressibility, flexibility and hydrophobicity/hydrophilicity.

A typical sponge suitable for use in the embodiments of the
5 invention has a distribution of pore sizes and preferably a mean pore size diameter of about 500 +/- 100 microns. This value has been reached by image analysis of several different synthetic sponges, and by making the assumption that the pores are spherical. Some suitable sponges may contain pores up to
10 3-4 mm in diameter, and sponges may also have pores so small that the image analysis technique could not detect individual pores.

The shape of cells within a sponge will depend upon the
15 process of manufacture, and can range from spherical to polyhedral in which the adjoining walls can vary from just above zero to almost 100% of the contact area, i.e. from essentially open meshworks to almost closed cells. Sponges prepared from fibrous materials can have no cells as such but
20 rather comprise a plurality of connected regions through which fluids can pass.

The cells in a sponge are preferably substantially intercommunicating, i.e. at least 50% by number of the cells
25 are intercommunicating. It is believed that this allows passage of materials through the body of the sponge, and the pore size is less than or equal to the diameter of the cell.

Sponges preferably comprise a harder abrasive layer, which may
30 be, for instance, impregnated or bonded onto the sponge. The abrasive material may be for example a firmer sponge, or synthetic fibres which may be interlinked e.g. Scotchbrite (TM). Such multipart sponges are known in the art.

- 7 -

Sponges may be hydrophilic or hydrophobic, but preferably the composition of the surface elements of the sponge should be capable of being water wetted. It is advantageous if both hydrophobic and hydrophilic properties were combined in a
5 single sponge such that the area of the sponge that contacted the skin is hydrophobic, whereas the area that contacted other surfaces is hydrophilic. It is believed that this reduces wetness of the hands and thus reduce contact with potentially irritant cleaning formulations thereby increasing the apparent
10 'mildness' of the cleaning formulation used.

Sponges currently sold for use in dish washing operations have average dimensions of 9x6.5x4cm (as length x width x depth) i.e. they are of a size to fit easily in the hand. These
15 often have at least one abrasive surface. More ergonomic versions are available with e.g. grooves for the fingers and these are suitable for use in embodiments of the present invention.

20 As will be show hereafter by means of examples a variety of commercially available sponges can be modified for use in the present invention either by folding the sponge and joining at least some of the abutting edges or by cutting an incision in one side of a sponge block.

25

Surfactant:

The surfactant containing composition can be a solid in the form of a block or powder, a gel or paste, or a liquid, any of which can contain or consist of the particulate phase. For the purposes of the present specification the term 'flowable' is used to describe powders and liquids. Compositions for use with embodiments of the present invention are generally
35 flowable.

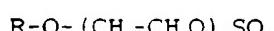
- 8 -

Surfactant content of solid block compositions for use in the method of the present invention is typically 5-20%wt.

- 5 Surfactant content of gel and paste compositions for use in the method of the present invention is typically 3-40%wt.
- Surfactant content of the flowable compositions for use in the method of the present invention is typically greater than 1%wt, preferably 2-50%wt, most preferably 2-10%wt

- 10 In a preferred embodiment of the present invention the surfactants include at least one anionic, zwitterionic or amphoteric surfactant. Particularly preferred surfactants include one or more of ethoxylated alkyl ether sulphate, lauryl sulphate and amido propyl betaine.

- 15 Amongst the most preferred surfactants are alkyl ether sulphates of the general formula:



- 20 where R is C₁₂₋₁₈ alkyl and n is 1 - 5. Preferably, R is lauryl-.

- 25 The alkyl ether sulphate surfactants are preferably present at a level of 2-30%wt. A particularly preferred surfactant is lauryl ammonium ether sulphate. Conveniently, this component is present in the formulations of the invention at levels of 2-20%wt, more preferably 3-7%wt on product for relatively dilute products or 8-18%wt for concentrates.

- 30 It is possible to use other anionic surfactant in combination with or to the exclusion of the ether sulphate surface active agents.

- 9 -

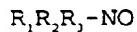
Anionic surfactants which may be used include alkylaryl sulphonates, alcohols sulphates, phosphate esters, sulphosuccinates, sulphosuccinamates, alkane sulphonates, olefin sulphonates, petroleum sulphonates, sarcosinates, 5 taurates, isethionates, and soaps. Particular examples of these classes of anionic surfactants include those sold under the trade names Eltesol SX30(TM) (sodium xylene sulphonate), Empicol L2(TM) (sodium lauryl sulphate), Triton H55(TM) (potassium phosphate ester), Marlinat DF8 (sodium 10 sulphosuccinate), Hostapur SAS 30X(TM) (sodium alkane sulphonate), Hostapur OS(TM) (sodium olefin sulphonate), Petronate S(TM) (sodium petroleum sulphonate), Hamposyl L30(TM) (sodium lauroyl sarcosinate), Fenopon T33(TM) (sodium N-methyl-N-oleyl taurate), and Fenopon AC 78(TM) (sodium 15 coconut isethionate).

Preferred amongst these surfactants additional are alcohol sulphates, particularly C₈₋₁₈ alcohol sulphates and alkyl benzene sulphonates.

20 Typical levels of alcohol sulphates in compositions of the present invention range from 5-15%wt on product, more preferably 6-10%wt on product.

25 Typical levels of alkyl benzene sulphonate in compositions of the present invention range from 10-30% on product.

It is possible to use nonionic surfactant in combination with the ether sulphates surface active agents. One particular 30 class of nonionic surfactants for use in combination with the ether sulphate surface active agents comprises the amine oxides of the formula:



- 10 -

in which R₁ is a long chain alkyl group, typically containing 8 to 20 carbon atoms; and R₂ and R₃ are the same or different, lower alkyl group, typically containing 1-4 carbon atoms.
Particular examples of this class of non-ionic surfactants are
5 alkyl dimethyl amine oxides such as sold under the trade name "Empigen OB" [TM] by Albright & Wilson.

Other classes of nonionic surface active agents which may be employed comprise polyalkoxylated fatty alcohols and their
10 esters; polyalkoxylated fatty acids; polyalkoxylated alkyl phenols; alkylamides; polyalkoxylated alkylamides, glucosides, polyglucosides, sucrose and sugar esters, fatty esters, ethoxylated alkylamides, ethoxylated long chain amines; alkyl amines, alkyl polyglucosides and alkyl
15 polyglycosides. Particular examples of these classes of nonionic surfactants are those sold under the trade names Synperonic A [TM] (alcohol ethoxylates), Crodet L24 [TM] (polyoxyethylene-24-lauric acid), Synperonic NP [TM] (nonyl phenyl ethoxylates), Empilan CME [TM] (coconut
20 monoethanolamide), Triton CG110 [TM] (alkyl glucoside), Glucam E10 [TM] (10 mole ethoxylate of methyl glucoside), Crodesta SL 40 [TM] (sucrose cocoate), Empilan MAA [TM] (ethoxylated coconut monoethanolamide), Ethomeen C12 [TM] (ethoxylated coconut amine), and Tagosoft 16B [TM] (cetyl isoctanoate).
25 Suitable amphoteric surfactants for use in combination with the ether sulphate surfactants include alkyl betaines, alkyl aminopropionates, alkyl iminodipropionates; alkyl glycinate; carboxyglycinate; alkyl imidazolines suiphobetaines; alkyl
30 polyaminocarboxylates and polyamphocarboxyglycinate. Particular examples of such amphoteric surfactants are those sold under the trade names Tegobetain A4080 [TM] (alkyl dimethyl betaine), Ampholax XCU [TM] (coco-amphoglycolate), Amphotensid CT [TM] (alkyl imidazoline based amphoteric),
35 Ampholax XCO 30 [TM] (coco-amphocarboxyglycinate) and Sandobet

- 11 -

SC[TM] (cocoamide-sulphobetaine); and sodium N-coco-aminopropionate, disodium N-coco-iminodipropionate, and cocoglycinate.

5 Preferred amongst these surfactants are betaines, preferably alkyl amido propyl betaines with an alkyl chain length of C₆-C₁₈. Coco amido propyl betaine is particularly preferred. Typical levels of betaine in compositions according to the present invention range from 0.5-5.0%wt, more preferably
10 1-3%wt on product.

Suitable cationic surfactants for use in the concentrates of the invention includes alkyl quaternary ammonium halides; primary, secondary and tertiary amines and their salts; and
15 polyamines. Particular examples of such cationic surfactants are those sold under the trade names Empigen BAC[TM] (alkyl dimethyl benz-alkonium chloride), Armac 1[TM] (tallow amine acetate-amine salts), Synprolam 35N3[TM] (N-alkyl propane propane diamine), and Synprolam 35X10[TM] (10 mole ethoxylated
20 primary amine).

It is preferable that the surfactant containing composition thickens on dilution with water. This can be achieved by the presence of an electrolyte in the surfactant composition.
25 Typically, the compositions of the present invention comprise at least one surfactant whose solution viscosity is strongly influenced by the prevailing electrolyte concentration. While other means by which the viscosity can be increased on dilution are known, the use of an electrolyte is preferred.
30 In preferred embodiments of the invention the thickening of the diluted composition is effected by the presence of selected surface active agents whose thickening effect, in the concentrate, is reduced by the presence of an excess of dissolved electrolyte. Thus, upon dilution of the
35 concentrate, the concentration of dissolved electrolyte is

- 12 -

reduced and the surface active agent component is then capable of exerting its thickening effect.

In embodiments of the invention, the combination of the
5 carrier and the composition is treated with water, either by dipping the combination into water or by the simple expedient of starting with a wet carrier. As a result of the dilution of the electrolyte which occurs, the electrolyte concentration falls below that which is sufficient to prevent the
10 surfactants from thickening and the viscosity of the surfactant composition rises. As described above, this increase in viscosity causes the surfactant and the particulate phase to be retained on the carrier and released over a significantly longer period of time.

15 Where the surfactants are sensitive to the presence of electrolyte, a broad range of electrolytes can be employed, provided that the electrolyte causes thickening of the surfactant at a first concentration and thinning of the
20 surfactant, relative to the viscosity peak at a second, higher concentration.

Preferred electrolytes of present inventions are NaCl, MgCl₂, MgSO₄, and mixtures thereof. Other water-soluble electrolytes
25 may be employed, including builders such as sodium, sodium phosphates and alkali metal silicates.

Typical electrolyte concentration is from 4.0 to 30% %w/w, preferred electrolyte concentration is from 4-15 %w/w,
30 particularly preferred concentration is from 4-10% %w/w.

As will be shown hereinafter by means of examples conventional surfactant-containing products which are known in the art of dishwashing can be used in embodiments of the present
35 invention.

Particulate phases:

- As mentioned above the sponge acts as a filter to retain particulate phases within the pouch or the body of the sponge.
- 5 Several particulate phases are envisaged in embodiments of the present invention. These preferably comprise abrasives, which are discussed in more detail below, encapsulated perfumes, builders, bleaches and/or microbiocides.
- 10 Suitable encapsulated perfumes are those available in the marketplace as 'Fresh and Clean' from the 3M company. As will be illustrated below by reference to examples the use of the encapsulated perfumes together with the sponge of the present invention significantly improves the persistence of the
- 15 perfume.

Typical average particle sizes for the particulate phase range from 1mm to 0.1 microns. The particulate phase can be wholly or partly water soluble.

20

Abrasive:

- Abrasives are optional components of the compositions for use
- 25 in the method of the present invention. Where abrasives are present the level of abrasive can range from 1-99% of the composition. The particulate abrasive is either insoluble in an aqueous phase or present in such excess that the solubility of the abrasive in an aqueous phase such as will be
- 30 encountered during the practice of the method of the invention is exceeded and consequently solid abrasive will exist in the composition when the aqueous phase is mixed with the composition.

- 14 -

Preferred abrasives for use in general purpose compositions have a Moh hardness below 6 although higher hardness abrasives can be employed for specialist applications.

5 Suitable abrasives can be selected from, particulate zeolites, calcites, silicas, silicates, carbonates, aluminas, bicarbonates, borates, sulphates, and, polymeric materials such as polyethylene. Of these the bicarbonates, borates and sulphates are soluble.

10 Preferred average (weight average) particle sizes for the abrasive fall in the range 0.5-200 microns, with values of around 10-100 microns being preferred. In this range an acceptable compromise between good cleaning behaviour and low substrate damage is achieved. However, as noted above, the sponge acts as a filter which prevents larger particles from contacting the surface and causing damage. This enables particles with a higher average particle size to be used.

15 20 Preferred levels of abrasive range from 5-99wt% on product, preferably in the range 20-40wt%, most preferably around 35wt% for liquid products. Such levels of abrasive give effective cleaning and good rinsing. For powder products moderately high levels of abrasive are used.

25 30 The most preferred abrasives are calcium carbonate (as calcite), mixtures of calcium and magnesium carbonates (as dolomite), sodium hydrogen carbonate, potassium sulphate, zeolite, alumina, hydrated alumina, feldspar, talc and silica. Calcite and dolomite are particularly preferred due to their low cost, hardness and colour.

As will be illustrated hereafter by reference to examples the surface damage associated with the use of an abrasive

- 15 -

component is significantly reduced in embodiments of the present invention.

5 Solvents:

In addition to the above-mentioned components compositions according to the present invention can comprise a solvent. Solvents are an optional component and are not essential to
10 the practice of the present invention.

Preferred solvents are selected from: propylene glycol mono n-butyl ether, dipropylene glycol mono n-butyl ether,
15 propylene glycol mono t-butyl ether, dipropylene glycol mono t-butyl ether, diethylene glycol hexyl ether, ethyl acetate, methanol, ethanol, isopropyl alcohol, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, n-methyl pyrrolidone and mixtures thereof.

20 The preferred solvents are propylene glycol mono n-butyl ether, dipropylene glycol mono n-butyl ether, ethanol, isopropyl alcohol, diethylene glycol monobutyl ether and mixtures thereof.

25

Minors:

The compositions of the invention can further comprise other non-essential components selected from the group comprising:
30 colours, whitening agents (such as titanium dioxide) and dyes, foam-control agents, preservatives (such as formaldehyde) and mixtures of one or more thereof.

35 Preferably the foam control agents comprise calcium sensitive soaps. Particularly preferred soaps are the C10-C18 saturated

- 16 -

or unsaturated fatty acids and salts thereof. Preferred levels of soap range from 0.1-2% of a fatty acid soap having C10-C18 carbon atoms. It is particularly preferred that the ratio of soap to total active should fall into the range:

5 1:5-1:20.

It is possible to include polymers in the composition of the invention. Guar gum is a suitable polymer. Typical inclusion levels of polymer range from 0.001-2%.

10

Hydrotropes are another optional component of the present invention. Ethanol is a suitable hydrotrope as are the xylene, cumene and benzene sulphonates. Preferably ethanol is present at a level of up to 10%wt, preferable up to a level of 15 6%wt.

Further optional components include an alkanolamine, preferably 1-10% of an alkanolamine, with levels of 2-6%wt being particularly preferred.

20

Particularly suitable alkanoamines include: 2-amino-2-methyl-1-propanol, mono-ethanolamine and di-ethanolamine. These materials are believed to give improved cleaning on tough or aged soils.

25

Preferred compositions according to the present invention comprise:

| | | |
|----|-------------|-----------------------------------|
| 30 | 2.0-10%wt | C8-C18 alkyl ether sulphate, |
| | 5.0-15%wt | C8-C18 alkly sulphate, |
| | 0.5-5.0%wt | C8-C18 alkyl amidopropyl betaine, |
| | 7.5-30.0%wt | electrolyte, and, |
| | up to 6%wt | ethanol |
| | to 100% | water and minors |

35

- 17 -

Other preferred compositions comprise:

2-15%wt C8-C18 alkyl ether sulphate,
3-16% wt alkyl benzene sulphonate (as the TEA salt)
5 7-14% wt alkyl benzene sulphonate (as the Na salt),
0.5-10%wt electrolyte, and,
0.5-10%wt hydrotrope.
to 100% water and minors

10 One particularly preferred composition according to the present invention comprises:

8-18%wt C8-C18 alkyl ether sulphate
0.5-5%wt amidopropyl betaine
15 0.5-10%wt electrolyte, and,
to 100% water and minors

In the last above-mentioned composition it is particularly preferred that the minors comprise:

20 0.01-1%wt guar gum
0.001-0.1%wt formaldehyde
0.001-0.1%wt butylated hydroxytoluene
0.1-5%wt perfume

25 In order that the present invention can be further understood it will be described hereafter with reference to the following non-limiting examples.

30

ExamplesExample 1: Surfactant Delivery.

5 The following examples were performed with clean plates. 2.0 gm of commercially available 'Persil' [TM] hand dishwashing liquid which was applied either to the surface of a damp 'Vileda Washmaid' [TM] sponge or placed in a pouch which had been cut into one face of an identical sponge with a sharp
10 knife. Such a sponge was thoroughly dampened by first immersing it in water and manually squeezing it until no more water could be expressed.

In control experiments, the sponge was placed on a clean white
15 ceramic dinner plate and 2gm of 'Persil' (a commercial 2:1 LAS/LES mixture having a cmc of about 0.01%w/v) was placed on the surface of the sponge, followed by 15ml of water. In a simulated cleaning action, the plate was kept flat on a table and rubbed in a circular direction ten times with the
20 surfactant-treated side of the sponge in contact with the plate.

The expressed liquid was collected from the plate using a glass filter funnel and the surfactant level in the collected
25 liquid was determined by hyamine titration. The plate was then rinsed, dried and the procedure repeated with the now slightly depleted sponge adding a further 15ml of water. This cycle was repeated twenty times.

30 The experiment was repeated using an identical sponge except that a slit had been cut into the sponge to form a pouch internally of the sponge. Instead of putting the surfactant product on the outer surface of the sponge, it was put into the pouch.

- 19 -

The concentrations of active measured in the two experiments are recorded in Table 1.1 below:

5

TABLE 1.1

| No. of "cleaning" cycles. | Conc. (%w/v) by titration using pouch sponge | Conc. (%w/v) by titration using surface of sponge |
|---------------------------------|--|---|
| 1 | 0.02 | 1.86 |
| 2 | 0.32 | 1.02 |
| 3 | 0.54 | 0.62 |
| 4 | 0.77 | 0.54 |
| 5 | 0.69 | 0.52 |
| 6 | 0.54 | 0.39 |
| 7 | 0.50 | 0.27 |
| 8 | 0.52 | 0.17 |
| 9 | 0.40 | 0.08 |
| 10 | 0.24 | 0.06 |
| 12 | 0.08 | 0.03 |
| 15 | 0.04 | 0.02 |
| 20 | 0.02 | 0.01 |

- 10 From the results given in Table 1.1, it can be seen that when applied to the surface of the sponge, most of the active is lost in the first few squeezes or plate washings. It is believed that the residual active distributes itself within the sponge and loss is then by simple dilution. The
- 15 log(active level) v. time or squeezes or plates washed graph is linear and calculation shows the exponent is proportional to the dilution factor.

- In contrast, when the pouch system was used, the amount of
20 surfactant delivered was low at first (although it was above

- 20 -

the critical miceile concentration of about 0.01 in this instance) and the level increased rapidly as more active reached the surface of the sponge, and then decay was similar to the surface dosed case. It is noted that the initial loss
5 of surfactant was avoided in the examples.

Example 2: Fragrance Persistence

- 10 The following experiments were performed with a hand diswash liquid base comprising:

| | |
|--|-------|
| Na Lauryl Ether Sulphate (Dobanol 23/3s) | 26.6% |
| Lauryl Amide Propyl Betaine | 3.8% |
| 15 Nonionic | 3.6% |
| LMEA | 2.0% |
| MgSO ₄ | 2.0% |
| EtOH | 1.5% |

- 20 The perfume used was 'Fresh and Clean' [TM] (ex 3M) which is available both in encapsulated and liquid form and was used in both forms.

The following method was developed to simulate a direct
25 application washing regime. A hand dishwash liquid containing a known concentration of perfume was applied directly to a dampened sponge, which was then used to wash a clean plate in a standard way. The plate was wiped 10 times in a circular motion, and then the sponge squeezed into 500ml of water 3
30 times. This procedure was repeated for 5 cycles. Comparison was made between pouch and surface application of the dishwash liquid, and the sponges were kept for further analysis as described below.

- 21 -

The following method was developed to simulate the use of a sponge during a dip and wipe dishwashing regime. A dish washing liquid containing a known concentration of perfume/capsules was either applied directly to the sponge or 5 diluted into 500ml of cold water in a Tergotometer pot to give a 1.0%AD solution. The sponge, either containing the dishwash liquid or not was then added to the pot and agitated in the Tergotometer for a known time. After the allotted time the sponges were squeezed to remove excess liquid and kept for 10 further analysis as described below.

Further analysis of the sponges was performed using an interval scaling technique. Sponges from the perfume capture/deposition experiments were each put into '8oz' glass 15 jars and left to equilibrate for at least an hour before asking panellists to sniff the jars and rank the perfume intensity along a linear scale from 0-20. Certain values along the scale had anchoring expressions as listed in Table 2.1 below:

20

Table 2.1

| Score | Anchoring Expression |
|-------|----------------------|
| | |
| 0 | No smell |
| 5 | Weak smell |
| 10 | Moderate |
| 15 | Strong |
| 20 | Very strong |

25

and a standard was always prepared consisting of a known mass of capsules or perfume and this was given a value of 15 ie strong on the scale. Ten panellists were recruited for each

set of tests. For experiments in which capsules were used, the sponge containing the capsules was put 3 times through a mangle to ensure all the capsules were broken. Visual examination under a microscope was used to confirm that all of 5 the capsules had broken after mangling. Duplicate standards were incorporated with the test samples as an indication of panellist ability to match odour intensities. Tests were performed in duplicate.

10 The perception of odour intensity within upper and lower boundaries (The upper limit being 'saturation' of the olfactory senses, and the lower limit being the limit of detection) was shown by Stevens to be proportional to the actual concentration raised to some power, which is a function 15 of the stimulus condition, and is known as the Stevens Law Exponent. The procedure used to estimate unknown test concentrations of perfume/capsules on sponges after treatment involved first determining the Stevens Law exponent. To this end, a 25ml solution containing a known mass of perfume or 20 capsules in either water or dilute (1%AD) hand dish wash liquid was applied to a fixed mass of sponge. The capsule samples were then put into plastic bags, sealed, and mangled three times. The sponges were subsequently put into randomly coded '8oz' glass jars and left for at least 1 hour to 25 equilibrate before presenting them to a panel to assess for odour intensity as described above. The liquid perfume samples were left in randomly coded '8oz' glass jars on a roller overnight before assessing. The perfume concentrations used were 0.01%, 0.05%, 0.1%, 0.2% and 0.4%. Knowing the 30 Steven's Law Exponent, and using a standard for comparison, it was possible to calculate the % of perfume retained on the sponge.

- 23 -

Table 2.2 shows the % of perfume captured after 10 minutes in a Tergotometer (simulating Dip & Wipe) as a function of perfume type and place of application of perfume.

5

Table 2.2

| Perfume Form | Pouch | Surface |
|--------------|-------|---------|
| Liquid | 53 | 10 |
| Capsules | 70 | 47 |

10

It can be seen from Table 2.2 that placing the perfume in a pouch enables more of either the capsules or the liquid perfume to be retained, compared to surface application. This is measured by perfume intensity, hence in the case of pouch application, the perfume scent is stronger, and can last longer on the sponge. It can be seen that the use of the particulate perfume within the sponge gives the largest benefit.

15

Table 2.3 shows the % of perfume captured after a Direct Application experiment as a function of perfume type and place of application of perfume.

25

Table 2.3

| Perfume Form | Pouch | Surface |
|--------------|-------|---------|
| Liquid | 70 | 11 |
| Capsules | 87 | 24 |

Again it can be seen from Table 2.3 that placing the perfume in a pouch enables more of either the capsules or the liquid perfume to be retained, compared to surface application of the composition to the sponge. It can again be seen that the use
5 of a particulate perfume within the pouch give the greatest benefit.

Example 3: Particle Filtering

10

Experiments were performed with a 'TESCO' (TM) cellulose sponge cloth (5.5 x 11.5 cm) which was folded and glued (using 'Superglue 4' (TM)) along the edges to form a pouch. The glued edges were stitched to re-inforce the glue joint.

15

1g of a commercially available dishwashing powder ('Vim' (TM) ex. Hindustan Lever India) was emptied into the pouch. The pouch was dampened and fixed to the head of a Sheen (TM) Linear Scrubbing Machine using the metal grips as supplied.

20

This apparatus was then used to 'clean' a sheet of aluminium for one minute with a mass of 1264g fixed to the head of the Sheen machine. After this 'cleaning' operation the aluminium sheet was rinsed under cold water and dried with compressed air prior to making measurements of the sheet with a 'Sheen

25

Trimicro Gloss Meter' (TM). A similar cleaning operation was performed in which the 'Vim' was applied to the outer surface of a double thickness of identical sponge and a third series of examples were performed simply with a dampened sponge. The glossmeter measurements were taken using a glossmeter which

30

had been calibrated with the standard supplied and on untreated material which had not been cleaned. All gloss measurements were taken at an angle of 20 degrees on the 'cleaned' areas and parallel to the direction of cleaning.

- 25 -

This whole series of experiments was then repeated using black perspex rather than aluminium.

Results for both sets of trials are shown in tables 3.1 and 5 3.2 below. The gloss values give are those for the untreated surface, that obtained by using a damp sponge and no surfactant or abrasive,

10

Table 3.1: results on aluminium

| Example | Surface gloss of untreated surface | Gloss after cleaning with Water only | Gloss after abrasive product using pouch | Gloss after abrasive product on surface of sponge |
|---------|------------------------------------|--------------------------------------|--|---|
| 3.1a | 113.0 | 122.2 | 78.4 | 17.0 |
| 3.1b | 116.8 | 121.5 | 75.9 | 18.0 |
| 3.1c | 118.4 | 120.6 | 74.6 | 18.4 |
| 3.1d | 118.6 | 125.6 | 78.2 | 17.3 |
| 3.1e | 119.0 | 123.3 | 87.7 | 16.1 |

15

TABLE 3.2: results on black perspex.

| Example | Surface gloss of untreated surface | Gloss after cleaning with Water only | Gloss after abrasive product using pouch | Gloss after abrasive product on surface of sponge |
|---------|------------------------------------|--------------------------------------|--|---|
| 3.2a | 79.2 | 79.7 | 71.6 | 30.5 |
| 3.2b | 79.2 | 79.6 | 72.8 | 33.4 |
| 3.2c | 79.1 | 79.8 | 72.4 | 33.2 |
| 3.2d | 79.2 | 80.0 | 72.8 | 31.3 |
| 3.2e | 79.1 | 80.0 | 70.8 | 28.4 |

- 26 -

These results show that there is less loss of gloss due to surface damage when the abrasive is delivered from within the pouch. However, as the surfactant was still delivered to the surface the cleaning benefits of surfactant were still
5 attained.

Example 4: Soil Transfer

- 10 The development of build-up during washing and it's dependency on active level was measured in a simulated cleaning process. A red dye was added to the soil and the build up of soil on the sponge monitored photometrically using a parameter a' as described below. In addition a panel of people was used to
15 visually estimate "dirtyness", and there was an almost linear correlation between on the one hand a' values relative to the clean sponge and on the other hand the magnitude estimation scores obtained from the panel.
- 20 As a measure of the potential for the built-up grease to transfer from the sponge to other surfaces, the sponge was pressed against white paper. The level of grease transferred was measured by the same photometric method. A commercial Persil (TM) type LAS/LES active system as described above was
25 used.

A model dishwash soil was prepared by heating together 2.5g stearic acid, 2.5g Priolene 6952 (fatty acid), 95.0g Mazola (TM) Corn Oil, and 0.12g Fat Red 7B, to 65°C. Separately, 200ml
30 of demineralised water were heated to 45°C, 100g of rice starch added and the mixture stirred. 800ml of boiling water was placed a large beaker and placed on a hot plate to keep it just boiling. The oil mixture was added to the starch mixture and stirred, then quickly but carefully added to the boiling
35 water, stirring continuously. 200 ml of water was used to

- 27 -

rinse out the beakers from the oil and starch, and the washings were added to the soil, which was allowed to cool to room temperature before use.

- 5 For each sample of dishwash liquid to be tested, five plates were each soiled with 5mls of soil as described above. The plates were soiled at a rate of one every 2.5 minutes, and 30 minutes ageing time elapsed between soiling and cleaning each plate. 3L dilutions of a 2:1 LAS:LES dishwashing liquid were
10 made up in cold water to provide a range of concentrations.

A sponge was immersed in the formulation, and squeezed several times to ensure that the sponge was primed, ie the formulation was evenly distributed throughout the sponge. Once the first
15 plate had been aged, it was cleaned using the sponge by wiping 10x in an anti-clockwise direction. The sponge was then rinsed under a vigorous flow of cold water, squeezing and rubbing until only one minute remained before the next plate was to be cleaned. The sponge was then squeezed tightly and
20 then re-immersed in the formulation. The sponge was then squeezed and released to re-prime the sponge, until it was time to clean the next plate.

After all five plates had been wiped, the sponge was rinsed
25 under the tap, and then put into a labelled plastic bag.

When all of the formulation samples had been used, the sponges were measured to determine how much fatty soil had been picked up by the sponge, using a "Dr Lange Micro Color" (TM). The
30 Dr Lange has a parameter, a' , which measures colour along the red-green axis. The more red, the more positive the value of a' , and the more green, the more negative the value of a' . Since the sponges used were green, and the dye used was red, the value of a' gave good discrimination between sponges. Each
35 sponge was measured five times, and the mean value of a'

- 28 -

calculated. Results are given as 'sponge colour' in Table 4.1 below.

Once the measurements had been made on the sponge, the sponge
5 was pressed by hand for a count of five onto a piece of white
filter paper, the amount of pink left on the white paper gave
an indication of the likelihood of re-deposition of fatty/oily
soil from the sponge onto surfaces being cleaned. Results are
give in Table 4.1 below.

10

Table 4.1 shows results obtained from this test for a range of
concentrations of 2:1 LAS:LES.

15

Table 4.1

| Conc (%) (surfactant) | Sponge Colour (a*) | Paper Colour (a*) |
|--------------------------|-----------------------|----------------------|
| 0 | 23.6 | 13.3 |
| 0.02 | 19 | 8.4 |
| 0.04 | 8.2 | 0.3 |
| 0.08 | 1.4 | 0 |
| 0.1 | -8.2 | -0.3 |
| 0.2 | -19.5 | -0.2 |
| 0.15 | -18.8 | |
| 0.5 | -29.7 | -0.2 |

Note: a* for clean sponge = -37

20 a* for white paper = 0

From Table 4.1 it can be seen that as active level fell below
0.1 - 0.2%AD build-up on the sponge increased quickly and
below about 0.04%AD transfer to the paper was obvious. In a
25 hot bowl wash the build up increases linearly with number of

- 29 -

plates cleaned. The delivery and build-up data can be combined to provide product performance comparison criteria based on the minimum level of active required to prevent soil build-up on the sponge or soil transfer. From the data given above for surfactant concentrations after a plurality of washing cycles it is possible to calculate the number of plates which can be washed before the surfactant level falls to a particular value. Results obtained for a plate wash test using the criteria listed are given in Table 4.2

10

Table 4.2

| Criterion | Pouch | Conventional |
|---|-------|--------------|
| a) No build-up on sponge i.e. conc > 0.15%AD | 11# | 1 - 7 |
| b) No transfer to paper i.e. conc > 0.05% | 12# | 1 - 10 |

15

= this discounts the first plate washed which appeared slightly streaky due to the lower starting surface concentrations.

20

From Table 4.2, it can be seen that the use of a pouch maintains the surfactant concentration in the effective range to prevent soil transfer and build-up on the sponge for more plate washes than use of a conventional sponge.

- 30 -

CLAIMS

5 1. A kit of parts comprising, in combination:

- 10 a) a shaped article comprising a sponge body having a first surface defining a pouch therein, said pouch being adapted to receive and retain a surfactant-containing composition, and,
- b) a surfactant-containing composition which comprises a particulate phase.

15 2. A method of surface cleaning using a sponge body having a first surface defining a pouch therein, said pouch being adapted to receive and retain a surfactant-containing composition which comprises the steps of:

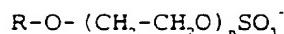
- 20 a) at least partially filling said pouch with a surfactant containing composition which comprises a particulate phase, and,
- b) performing a manual cleaning operation with the
- 25 sponge.

3. An article according to claim 1 or a process according to claim 2 wherein the sponge has a mean pore size diameter of about 500 +/- 100 microns.

- 30 4. A method according to claim 2 wherein the surfactant containing composition is a flowable composition comprising 2-50%wt surfactant.

- 31 -

5. A method according to claim 2 wherein the surfactant comprises alkyl ether sulphate of the general formula:



5

where R is C₈₋₁₈ alkyl and n is 1 - 5.

- 10 6. A method according to claim 2 wherein the surfactant containing composition thickens on dilution with water.
- 10 7. A method according to claim 2 wherein the surfactant containing composition comprises an abrasive.
- 15 8. A method according to claim 2 wherein the surfactant containing composition comprises an encapsulated perfume.
- 15 9. A method according to claim 2 wherein the average particle sizes for the particulate phase is from 1mm to 0.1 microns.

20

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/EP 97/06960

| | | | | |
|---|---|--|--------------------|--|
| A. CLASSIFICATION OF SUBJECT MATTER | | | | |
| IPC 6 C11D17/04 C11D1/94 C11D1/37 C11D3/20 C11D3/50 A47L13/17 | | | | |
| According to International Patent Classification (IPC) or to both national classification and IPC | | | | |
| B. FIELDS SEARCHED | | | | |
| Minimum documentation searched (classification system followed by classification symbols) | | | | |
| IPC 6 C11D A47K A47L | | | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | | | |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used) | | | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | | | |
| Category | Citation of document, with indication, where appropriate, of the relevant passages | | | Relevant to claim No. |
| X | US 4 847 089 A (KRAMER DAVID N ET AL) 11 July 1989 see column 4, line 59 - column 6, line 60; column 7, line 66 - column 8, line 2; examples 3,8; claim 1 --- | | | 1-3,7-9 |
| X | GB 897 284 A (AMON R) 23 May 1962 see page 1, lines 32-40; page 2, lines 24-34 --- | | | 1,2 |
| A | WO 96 32464 A (UNILEVER PLC ;UNILEVER NV (NL)) 17 October 1996 see page 6, line 1 - page 12, line 15; claims 1-10 --- | | | 4-6 |
| A | EP 0 141 863 A (FREUDENBERG CARL FA) 22 May 1985 see page 6, line 25 - page 9, line 28 --- | | | 1,2 -/- |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. | | | | |
| * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family | | | | |
| 1 | Date of the actual completion of the international search | | | Date of mailing of the international search report |
| | 17 April 1998 | | | 06/05/1998 |
| Name and mailing address of the ISA | | | Authorized officer | |
| European Patent Office, P B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 eoo nl. Fax: (+31-70) 340-3016 | | | Ainscow, J | |

INTERNATIONAL SEARCH REPORT

| |
|---|
| International Application No PCT/EP 97/06960 |
|---|

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | US 3 775 014 A (ROSBORNE J) 27 November 1973 see entire document --- | 1,2 |
| A | US 4 330 220 A (SCHAAR CHARLES H ET AL) 18 May 1982 see entire document --- | 1,2 |
| A | US 4 789 262 A (SANCHEZ THEOLINDE) 6 December 1988 see entire document ----- | 1,2 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

| | |
|--|------------------------------|
| | International Application No |
| | PCT/EP 97/06960 |

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|--|------------------|---|--|--|
| US 4847089 A | 11-07-89 | US 4941989 A US 5620527 A | | 17-07-90 15-04-97 |
| GB 897284 A | | NONE | | |
| WO 9632464 A | 17-10-96 | BR 9501520 A BR 9502064 A AU 5273796 A CA 2215795 A EP 0820503 A | | 19-08-97 26-08-97 30-10-96 17-10-96 28-01-98 |
| EP 0141863 A | 22-05-85 | DE 3327805 A | | 21-02-85 |
| US 3775014 A | 27-11-73 | NONE | | |
| US 4330220 A | 18-05-82 | AR 224308 A AU 540506 B AU 7062081 A BE 589209 A BR 2103398 A CA 1182956 A DE 3120446 A FR 2484236 A GB 2080100 A, B JP 1676111 C JP 3039706 B JP 57029369 A ZA 8103247 A | | 13-11-81 22-11-84 17-12-81 01-10-81 24-02-82 26-02-82 15-04-82 18-12-81 03-02-82 26-06-92 14-06-91 17-02-82 26-05-82 |
| US 4789262 A | 06-12-88 | NONE | | |